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EXTRACTION CHROMATOGRAPHY WITH LIQUID ION EXCHANGERS AS STATIONARY PHASE

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SUMMARY

The use of Kel-F (polytrifluorochloroethylene) and Microthene-710 (microporous polyethylene) supporting some liquid ion exchangers is described. Solutions of tri-*n*-octylamine (TNOA), Aliquat-336 and di(2-ethylhexyl)phosphoric acid (HDEHP) have been used as stationary phases.

Many separations were carried out both by column chromatography and by batch extraction. This technique can be used successfully as a selective pre-concentration step for the determination of many radionuclides in aqueous solutions and biological samples.

The possibility of supporting an organic redox agent together with the liquid ion exchanger is also described.

Finally, the possible advantages of this technique when used in connection with liquid scintillation counting are discussed.

INTRODUCTION

Many analytical separations have been obtained in our laboratory by supporting liquid ion exchangers (tri-*n*-octylamine, TNOA; a quaternary ammonium salt, Aliquat-336; di(2-ethylhexyl)phosphoric acid, HDEHP) on microporous polymers such as polytrifluorochloroethylene (Kel-F) and microporous polyethylene (Microthene-710)¹⁻³. This paper summarizes some practical applications of this technique. In addition, the advantages of supporting a redox agent together with the extractant and of using extraction chromatography in connection with liquid scintillation counting are discussed.

EXPERIMENTAL AND RESULTS

Choice of the inert support

Six commercially available microporous polymeric compounds were considered¹, *viz.*, Kel-F, Microthene-710, Algoflon (polytetrafluorochloroethylene), Moplen (isotactic polypropylene), Vipla (polyvinyl chloride) and Corvic (polyvinyl chloride-polyvinyl acetate copolymer). All of these materials gave good results as supporting

agents; Kel-F was used in the first experiments, but it was then replaced with Microthene-710 because of its lower cost and ready availability.

Extraction chromatography with liquid anion exchangers

Separation of Fe(III)-Co(II)-Ni(II) in aqueous solutions with a Kel-F-TNOA column¹. The feeding solution is 8 M HCl. Nickel is not retained, cobalt is eluted with 2 M HCl and iron(III) with 1 M HNO₃.

Separation of U-Th in aqueous solutions with a Kel-F-Aliquat-336 column¹. When a 4 M HNO₃ feeding solution is used, uranium is not retained and thorium can then be eluted with 8 M HCl. When the feeding solution is 8 M HCl, thorium is not retained and uranium can then be eluted with 0.5 M HNO₃.

Determination of plutonium in urine with a Kel-F-TNOA column⁴. After co-precipitation of plutonium with magnesium and calcium phosphates, the precipitate is dissolved in 2 M HNO₃ and the solution is percolated through a Kel-F-TNOA column. After washing with 1 M HNO₃, the radionuclide is eluted by reduction to Pu(III) with H₂SO₃. Plutonium is then electroplated and counted with a solid-state detector for alpha-particles. The final yield is 90.5% and the sensitivity limit is 0.04 pCi for a 24-h urine sample.

Extraction chromatography with HDEHP liquid cation exchangers

Separation of Am-Pu in aqueous solutions with a Microthene-HDEHP column. The column consists of Microthene supporting 50% HDEHP in xylene. Both the radionuclides are retained on the column in 0.05 M HNO₃ solution; americium is then eluted with 1 M HCl and plutonium(IV) with 12 M HCl, as shown in Fig. 1.

Determination of Sr-90 in urine with a Microthene-HDEHP column⁵. This method is based on the retention of yttrium-90 at its equilibrium with strontium-90 on a column of Microthene supporting 1.5 M HDEHP in toluene. The urine is wet mineralized with HNO₃ and the pH is brought to 0.5; the solution is percolated through the column; strontium-90 is not retained and, after washing, the isolated yttrium-90 can then be eluted with 6 M HNO₃.

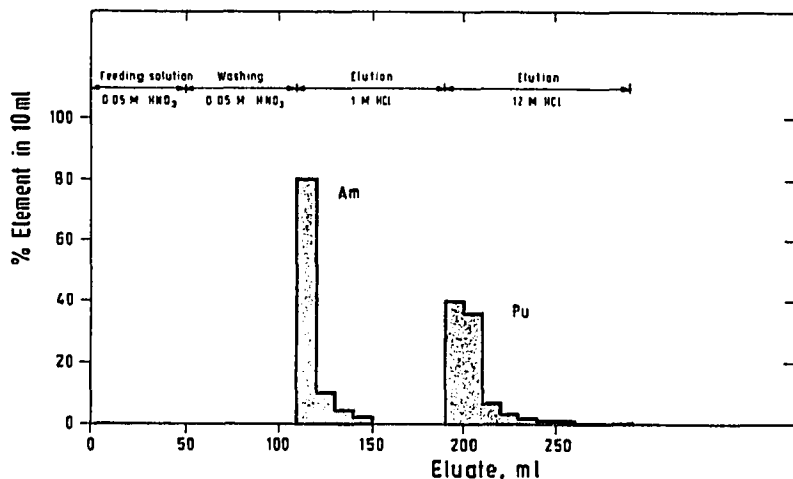


Fig. 1. Separation of Am(III)-Pu(IV) with a Microthene-HDEHP column.

Yttrium is precipitated as yttrium oxalate at pH 1.5 and counted in a low-background beta-detector. The final yield is 92% and the sensitivity limit is 5 pCi for a 24-h urine sample.

*Determination of Fe-55 in fall-out samples with a Microthene-HDEHP column*⁶. After the isolation of uranium, thorium and plutonium obtained by passing 7.5 M HNO₃ through an anion-exchange resin, the eluate containing iron-55 is immediately percolated through a Microthene-HDEHP column; iron is retained on the column and can be eluted with 6 M HCl. After an electroplating procedure, iron-55 is determined by counting its X-ray emission.

*Determination of Am-241 in urine by a batch extraction with Microthene-HDEHP*⁷. After wet mineralization of the urine with HNO₃ and H₂O₂, the pH is brought to 3 with ammonia solution; a batch extraction of the americium is then performed by stirring the urine solution with Microthene-HDEHP for 45 min. The slurry is transferred to a chromatographic column; after washing with 0.001 M HNO₃, americium is eluted with 3 M HNO₃, electroplated and alpha-counted with a solid-state detector. The final yield is 85.9%, the sensitivity limit is 0.04 pCi and the decontamination factors from the other alpha-emitters are as follows: 70 from thorium, 60 from protactinium, 80 from uranium and 100 from neptunium and plutonium.

Fig. 2 shows the americium-241 extraction as a function of pH (no DTPA curve); some extraction curves with urine containing diethylenetriaminopentaacetic acid (DTPA) are also reported. The results show that a sufficient recovery of americium-241 can also be obtained from urines of persons treated with this chelating agent for therapeutic reasons⁸.

Column redox-extraction chromatography

The possibility of supporting an organic redox compound together with the extractant was studied. When a solution of iron(II) in 6 M HCl is passed through a

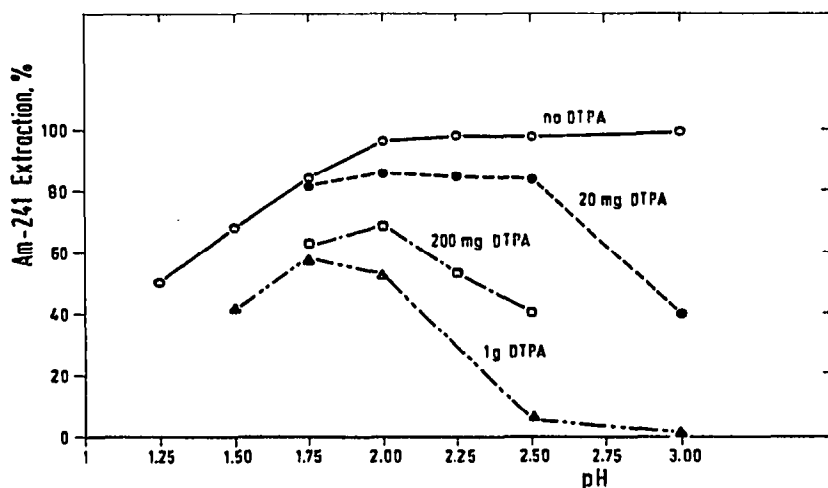


Fig. 2. Batch extraction of Am(III) in urine with a Microthene-HDEHP slurry as a function of pH and DTPA concentration.

column of Microthene supporting TNOA and tetrachlorohydroquinone (TCHQ), iron is in the iron(II) form and is not retained on the column. When the same solution is passed through a TNOA-tetrachloroquinone (TCQ) column, iron(II) is oxidized to iron(III), which remains on the column in the form of an anionic hydrochloride complex (Fig. 3).

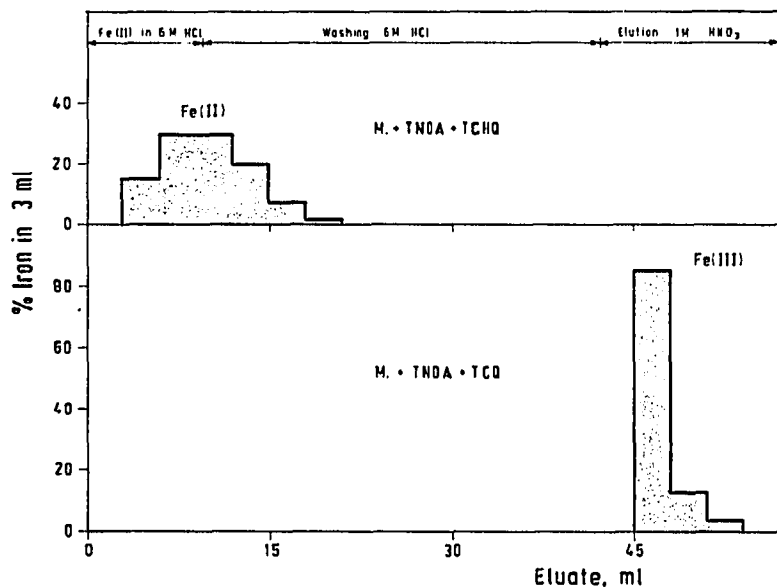


Fig. 3. Elution diagram of Fe(II) with a Microthene-TNOA-TCHQ column and with a Microthene-TNOA-TCQ column.

Some separations of actinide elements have been obtained by supporting, together with the extractant tri-*n*-octylphosphine oxide (TOPO), some reducing agents such as tetrachlorohydroquinone, 2,5-dichloronaphthaquinone, 2,5-di-*tert.*-butylhydroquinone and 2,5-di-*tert.*-phenylhydroquinone (DTPHQ). These compounds can reduce plutonium(IV) and plutonium(VI) to plutonium(III) and neptunium(V) and neptunium(VI) to neptunium(IV).

By using a Microthene-TOPO-DTPHQ column, the quantitative separations plutonium(III)-neptunium(IV), plutonium(III)-uranium(VI) and americium(III)-neptunium(IV) in 6 *M* HCl were obtained⁹. Fig. 4 shows the behaviour of plutonium and neptunium in 6 *M* HCl with a Microthene-TOPO column and with a Microthene-TOPO-DTPHQ column.

Extraction chromatography and liquid scintillation counting

By using this type of chromatography, it is possible to avoid the elution of alpha- or beta-emitters from the column if a liquid scintillation counting step is introduced. In fact, a Microthene-TNOA or Microthene-HDEHP slurry containing the extracted radionuclide can be transferred into a scintillation vial; the scintillation liquid is then added and the counting is carried out. The counting yields are good, as

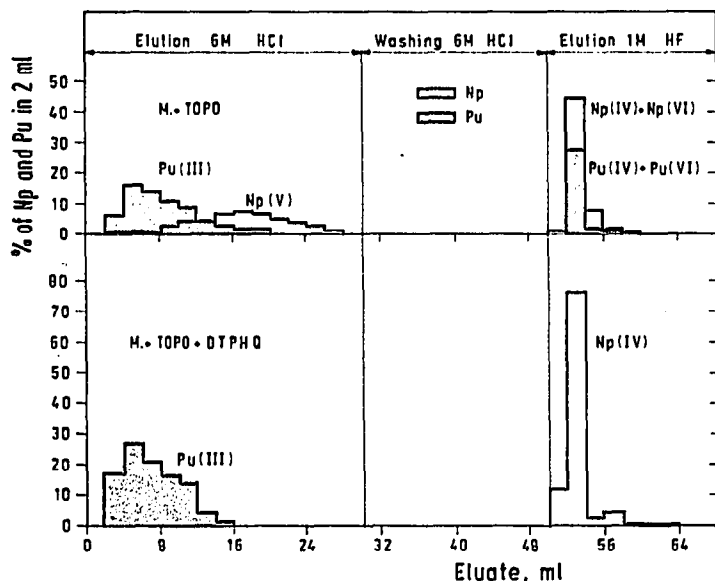


Fig. 4. Separation of Pu-Np with a Microthene-TOPO column and with a Microthene-TOPO-DTPHQ column.

shown in Table I; the background is about 15 c.p.m. Similar results could not be obtained with ion-exchange resins. Work is now in progress to prepare some extraction-scintillating columns by supporting an insoluble scintillating compound together with the extraction agent.

TABLE I

LIQUID SCINTILLATION COUNTING OF THE COLUMN AFTER ADDITION OF 10 ml OF INSTA-GEL

Radionuclide	Column	Aqueous solution	Counting yield (%)
Pu-239 (α)	3.5 g Microthene + 2.5 ml TNOA	2 M HNO ₃	91.6
U-233 (α)	3.5 g Microthene + 2.5 ml TNOA	6 M HCl	94.2
Am-241 (α)	3.5 g Microthene + 2.5 ml HDEHP	0.001 M HNO ₃	97.6
Y-90 (β)	3.5 g Microthene + 2.5 ml HDEHP	0.3 M HNO ₃	90.0
U-233 (α)	3.5 g Dowex 1-X2	6 M HCl	19.2
U-233 (α)	3.5 g Dowex 2-X10	6 M HCl	10.0

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